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Technical Reports 60 to 63
Laboratory for Insulation Research
Massachusetts Institute of Technology

February, 1953

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S. C. Abrahams

Laboratory for Insulation Research
Massachusetts Institute of Technology
Cambridge, Massachusetts

O. N. R. Contracts N5ori-07801
N5ori-07858

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Abstract: 2, 2-Dinitropropane forms face-centered, cubic crystals at room temperature, with $a_o = 8.78 \pm 0.05$Å, and 4 molecules per unit cell. Molecular disorder is necessarily present in the cell, and several models are examined. Excellent agreement is obtained with a model in which the molecule possesses complete orientational disorder. Although the distinction between "rotational" disorder in time and in space is not possible, the following mechanism is suggested: while the disorder is complete at long range, there is a high degree of order at short range.

Introduction

Dielectric constant and heat capacity studies of several tetra-substituted methanes just below their m.p. have been taken as indicating rotational freedom in the solid state.[1] A recent study of the dielectric constant and loss of 2, 2-dinitropropane[2] shows that the rotator phase has a dielectric relaxation time corresponding to a wavelength close to 3 cm. at room temperature. Nuclear magnetic resonance measurements on this crystal indicate that the methyl hydrogens have rotational motion in the plane of the protons at an effective frequency greater than 10^4 cps above ca. -180°C.[3] No X-ray investigation of this compound, apparently, has previously been undertaken, and the present study is an attempt

1) R. W. Crowe and C P. Smyth, J. Amer. Chem. Soc. 72, 4009 (1950).
2) J. G. Powles, D. E. Williams, and C. P. Smyth, J. Chem. Phys.; to be published.
3) J. G. Powles, private communication.

to describe the nature of the disorder in this crystal at room temperature.

Experimental

With slow sublimation (about 6 months) 2, 2-dinitropropane forms well-shaped plates, which plastically deform when handled. A simple technique was devised for preparing single crystals, in which melted 2, 2-dinitropropane was admitted into a capillary open at both ends. On cooling, the resulting clear glass-like solid was generally found to be a single crystal. This frequently ruptured later with the formation of bubbles within the crystal. The X-ray data were obtained by means of Laue, rotation and precession photographs, using Mo and Cu radiations. The intensities were estimated visually from a set of multiple exposure precession camera films.

Crystal Data

2, 2-Dinitropropane, $C_3H_6N_2O_4$, forms colorless, waxy, plastic crystals, which melt at 53°C and undergo a transition at – 7°C. The crystal belongs to the cubic system, with $a_o = 8.78 \pm 0.05$ Å, the only systematic absences being $hk\ell$ with $h + k = 2n + 1$, $k + \ell = 2n + 1$ and $h + \ell = 2n + 1$. Piezoelectric tests are negative. Thus the only possible space groups allowed are F23, F432, $F\bar{4}3m$, Fm3 and Fm3m, of which only the last two possess a center of symmetry. The measured density is 1.30, and the calculated, 1.32. There are four molecules per unit cell.

Analysis of the Disorder

The symmetry possessed by each of the five possible space groups requires, in the case of the least amount of disorder, that the methyl and nitro groups occupy identical positions, with the central carbon atom at the origin. Thus the two carbon and the two nitrogen atoms lie either at $x\ x\ x$, $x\ \bar{x}\ \bar{x}$, $\bar{x}\ x\ \bar{x}$, $\bar{x}\ \bar{x}\ x$ if the space group is noncentrosymmetric, or at $x\ x\ x$, $x\ \bar{x}\ \bar{x}$, $\bar{x}\ x\ \bar{x}$, $\bar{x}\ \bar{x}\ x$,

$\bar{x}\,\bar{x}\,\bar{x}$, $\bar{x}\,x\,x$, $x\,\bar{x}\,x$, $x\,x\,\bar{x}$ if the space group is centrosymmetric. This, of course, is merely stating that the tetrahedral bond distribution about the central carbon atom is being used by the crystal symmetry (Fig. 1).

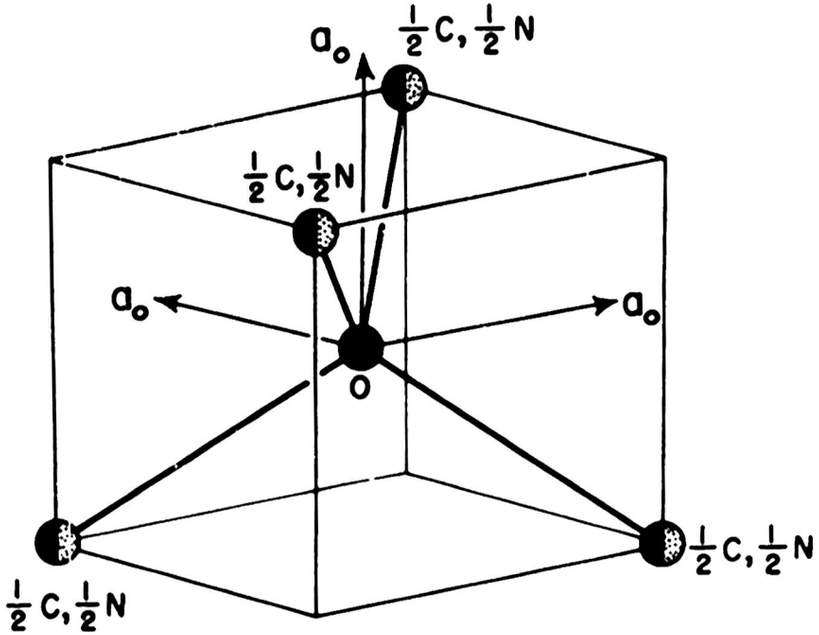
The following molecular dimensions are used in all models: C – C and C – N = 1.51Å, C – H = 1.09Å, N – O = 1.23Å, O – $\hat{N}$ – O = 125°, H – $\hat{C}$ – H, C – $\hat{C}$ – C, and N – $\hat{C}$ – N = 109.5°. In the first four models the hydrogen atoms of the methyl groups are taken as rotating in the plane of the hydrogen triangle[3]. The atomic scattering factors given by James and Brindley[4] were used, with a temperature factor correction of $\exp\left[-B\left\{(\sin\theta)/\lambda\right\}^2\right]$, where $B = 5\text{Å}^2$.

In the first model considered, the space group was assumed to be centrosymmetric. The oxygen atoms were taken as fixed with respect to the rest of the molecule, and each atom must then occupy at least three possible positions (cf. the 96-fold position in Fm3 and Fm3m). One oxygen atom was placed in the eclipsed position with respect to the three other groups linked to the central carbon atom. The second oxygen atom then necessarily occupied the staggered position. The geometrical structure factor for the carbon and nitrogen atoms is then $8 \cos 2\pi hx \cos 2\pi kx \cos 2\pi lx$, and for the oxygen atoms is $8/3\,[\cos 2\pi hx \cos 2\pi ky \cos 2\pi lx + \cos 2\pi hx \cos 2\pi kx \cos 2\pi ly + \cos 2\pi hy \cos 2\pi kx \cos 2\pi lx]$. For the hydrogen atoms it is $24 \cos 2\pi hx \cos 2\pi kx \cos 2\pi lx\, J_o(t)$, where the center of the hydrogen atom orbit is at x x x, and $J_o(t)$ is the zero order Bessel function, with $t = \frac{2\pi\rho}{d} \sin\alpha$, ρ being the radius of the orbit, α the angle between the planes of the orbit and of the reflection, and d the spacing.[5] The calculated structure factors for this model are listed in Table 1 under F1. The structure factors for the non-centrosymmetric case of this model are found under |F2|. The geometrical structure factors for this case are very simply related to those already given. Since it has not been established by other means whether or not the nitro group is also rotating, this

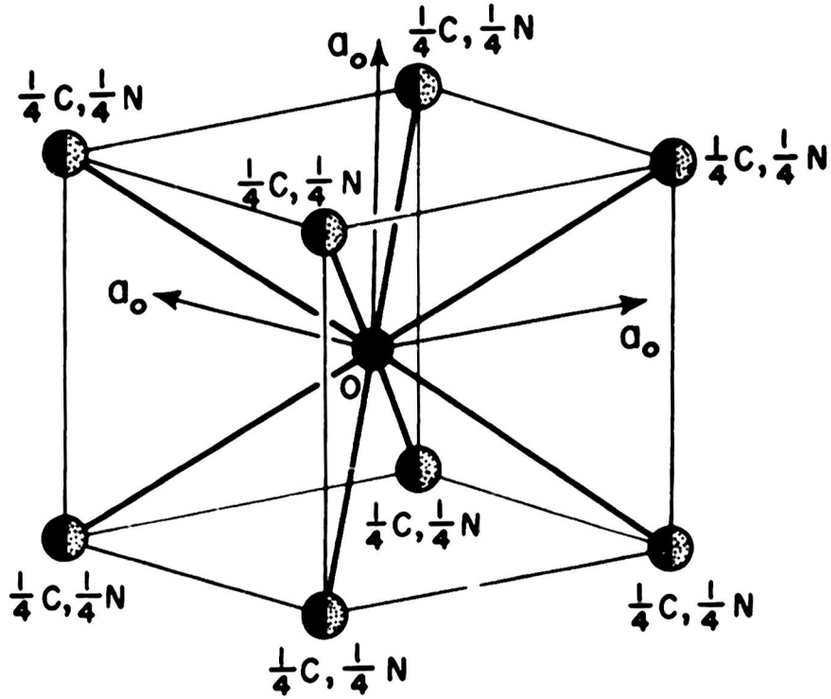
4) R. W. James and G. W. Brindley, Z. Krist. 78, 470 (1931).

5) J. M. Bijvoet, and J. A. A. Ketelaar, J. Amer. Chem. Soc. 54, 625 (1932).

Fig. 1. (a) A tetrahedral distribution of the carbon and nitrogen atoms, with averaged weights, in the non-centrosymmetric, face-centered cubic space groups; (b) An octahedral centrosymmetric distribution. Solid circles represent carbon, and shaded circles nitrogen atoms.



(a)



(b)

possibility was next considered for both centrosymmetric and noncentrosymmetric space groups. The structure factors corresponding to this case are listed, respectively, under F3 and |F4|.

The maximum molecular disorder which could be present in this crystal gives each atom an equal chance of being at any point on the surface of a sphere, with radius the interatomic distance between that atom and the center of rotation. This would be equivalent to complete rotational disorder, at least, statistically. The geometrical structure factor for a group such as this is $(n_j \sin r_j s)/r_j s$,[6] where n_j = number of jth atoms, r_j = radius of the jth sphere (the center of the sphere being at the origin of the cell), and $s = (4\pi \sin \theta)/\lambda$. The central carbon atom is almost exactly at the steric center of the molecule, since the C—H distance is 2.32Å and the C—O distance is 2.34Å. The structure factors for a rotational disorder model with the central carbon atom at the rotation center are given in Table 1 under F5. An alternative center of rotation is the center of inertia,* 0.57Å from the central carbon atom. Structure factors for the rotational model with this as center are collected under F6.

The agreement between observed and calculated structure factors in Table 1 is uniformly better for the centrosymmetric case than for the noncentrosymmetric (the rotating models are centrosymmetric). It thus seems likely that the positions 0 0 0, $0\ \frac{1}{2}\ \frac{1}{2}$, $\frac{1}{2}\ 0\ \frac{1}{2}$, $\frac{1}{2}\ \frac{1}{2}\ 0$ are centers of symmetry.

Discussion

In considering a structure model for a crystal such as 2, 2-dinitropropane in which some disorder must necessarily be present, the small number of observations imposes a severe limitation. Although very many models may be set up, the usual methods of refinement associated with ordered structures are

6) R. W. James, "The Optical Principles of the Diffraction of X-Rays," G. Bell and Sons, London, 1948, p. 467.

*The writer is indebted to Dr. W. N. Lipscomb for suggesting this alternative.

Table 1. Structure factors *for the disordered models of 2, 2-dinitropropane.

hkl	F1	|F2|	F3	|F4|	F5	F6	F_{obs}
111	+ 94	65	+ 97	65	+ 125	+ 113	116
200	+ 35	20	+ 29	15	+ 46	+ 58	55
220	− 3	1	+ 19	10	− 8	− 5	6
311	− 12	33	− 7	20	− 8	− 10	7
222	+ 19	50	+ 8	64	− 5	− 8	7
400	− 25	14	− 27	14	+ 3	− 1	5
331	+ 15	16	+ 12	14	+ 4	+ 3	5

*In this table, $\sum|F_{hkl}|$ in all columns has arbitrarily been placed equal to 200.

no longer available, with a consequent loss of detail.[7] Between the four models based on minimum disorder, and the rotational disorder models, an infinity of other models is possible. The agreement of the statistical-rotating model structure factors with the observed values is so good for both centers of rotation, however, that it seems unlikely that the true model would be very different from this. If the molecules may now truly be represented as spheres, with the central carbon atom at the center, the closest approaches between nearest neighbors could be 1.5Å. For the center of inertia at the center of the sphere, this approach could be 0.9Å. The density is fairly high at 1.32 gm cm^{-3}, but there is no apparent reason why any intermolecular contact should be much less than ca. 2.9Å. It thus seems virtually certain that interaction between neighbors must occur. A simple mechanism which would provide for this interaction is that, while the disorder is complete at long range, at short range there is a high degree of order. In this case the closest contacts could be about 2.8Å.

It is of interest to note that carbon tetrabromide, in the transition range just below the m.p, has been reported as giving good agreement between the ob-

7) Cf. S. C. Abrahams and W. N. Lipscomb, Acta Cryst. 5, 93 (1952).

served intensities and those calculated for a rotational disorder model.[8] Similar behavior has also been observed in carbon tetrachloride.[9] However, Marshall, Hart and Staveley[10] state that their specific heat measurements indicate that the carbon tetrabromide molecules do not freely rotate in the high temperature form.

Acknowledgments

The writer wishes to thank Dr. J. G. Powles, University of Illinois, for bringing this problem to his attention, and for a gift of 2, 2-dinitropropane; and also Professor A. von Hippel for his interest.

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8) C. Finbak, Tids. Kjemi. Bergvesen, 17, No. 9, p. 145 (1937).

9) R. L. Collin, private communication.

10) J. G. Marshall, K. R. Hart, and L. A. K. Staveley, Nature, 168, 519 (1951).